

Questa Baseline and Pre-mining Ground Water Investigation:11. Geochemistry of Composited Material from Alteration Scars and Mine-Waste Piles

Performed in Cooperation with the New Mexico Environment Department

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Abstract

Composited, surficial material was collected from alteration scars, a less intensely altered site, and mine-waste piles. All samples were analyzed for forty elements by inductively coupled plasma-atomic emission spectrometry, total sulfur and quantitative X-ray diffraction. This work was performed in cooperation with the New Mexico Environment Department.

Introduction

The Questa molybdenum mine, located in the southern Sangre de Cristo Range in north central New Mexico, is in the process of developing a mine-closure plan. This report is one of a series of reports that is being published by the U.S. Geological Survey (USGS) to evaluate the geochemical baseline and pre-mining ground-water quality of the Red River Valley Basin, New Mexico. As part of this study, composite samples of solid materials were collected from nine natural alteration scars both proximal to and on the Questa Molybdenum mine site in September 2001 and September 2002. For comparison with the alteration scar samples, a composite sample was collected from a less intensely altered (dominantly propylitic alteration) site in September 2001. Samples of solid composite materials were also collected from five of the major mine-waste piles on the Questa Molybdenum mine site property in September and November 2002. A topographic map shows the sampling site locations in figure 1.

Site Overview

The relief of the study area in the southern Sangre de Cristo Range in north central New Mexico is characterized as steep, ranging from approximately 2400 m on the Red River to over 2900 m at the higher elevations on the mine site. There are numerous intermittent tributaries including Hansen, Straight and Hottentot Creeks that drain into the Red River. The Red River Valley between the towns of Red River and Questa is vegetated with a mix of cottonwood trees (at the river's edge) and piñon pine, juniper, ponderosa pine and Douglas fir forest depending on slope aspect and elevation.

The climate of the area is semi-arid with hot summer days, localized, heavy thundershowers (especially in the months of July and August), and cool summer nights. Winters are mild with the higher elevations, receiving the over 600 cm of snowfall per year (there is even a small ski resort in the town of Red River).

The geology of the area is complex and best described by numerous authors that have studied and written the geological history (see for example Carpenter, 1968, Reed and others, 1983, Lipman, 1988, Meyer and Leonardson, 1990 and Czamanske and others, 1990, to name a few). As a result of the intense hydrothermal alteration and weathering, unique alteration scars have developed on the landscape. The majority of the alteration scars are located north of the Red River both on and off the mine site and east

of the mine site toward the town of Red River, New Mexico (see fig.1). These scars are characterized by deep incised valleys that developed as a result of high rates of weathering and erosion during snowmelt in the spring and intense thunderstorms in the summertime (Meyer and Leonardson, 1990; Shaw and others, 2002).

Methods

Composite Sampling Method

The sampling strategy for collecting surficial material was modified from a method developed by Smith and others, 2000. To get a representative sample for this study, a composite from each site consisting of a minimum of thirty subsamples or intervals of surficial material was taken from the surface to no deeper than 15 cm using a common stainless steel garden trowel. Because a complete sampling of an alteration scar or mine-waste pile was physically impossible, a strategy was adapted. In drainages, a subsample was collected from the creek bottom, and on alteration scars and mine-waste piles, samples were collected along -traverses - (see fig. 1). Each subsample was taken randomly every 20 paces and particles greater than pebble size (approximately 1 cm) were not collected. Approximately 100 g of material were taken at each interval and placed in a five gallon plastic bucket. The composite samples were brought back to the USGS offices in Denver, air dried, mixed and dry sieved to less than 2 mm. The final composite sample of less than 2 mm weighed at least 1 kg.

Nine alteration scar composites were collected from the following sites: SW Hansen, Hansen Creek, Straight Creek, SE Straight, Hottentot Creek, June Bug, Goat Hill, Sulphur Gulch and W Goat Hill. One less intensely altered composite was collected in the next drainage (unnamed) west of SW Hansen Creek. Figures 2a and 2b are representative photos of two alteration scars that were sampled in this study.

Five mine-waste pile composites, were collected from the following sites: Sugar Shack West, Sugar Shack South, Sugar Shack Middle, Old Sulphur Gulch and Capulin A single traverse of the top bench was sampled for the composite taken from Capulin waste pile. A single traverse along the base of Sugar Shack West waste pile was sampled for the composite. Three traverses were sampled (the base and two benches) for the Sugar Shack South, Sugar Shack Middle and Old Sulphur Gulch composites. The three traverse composites were combined to make one representative composite for each of these waste piles. These composite samples are representative of 72% of the total waste rock produced at the mine site. Figures 3a and 3b are photos of the mine waste piles closest to the Red River.

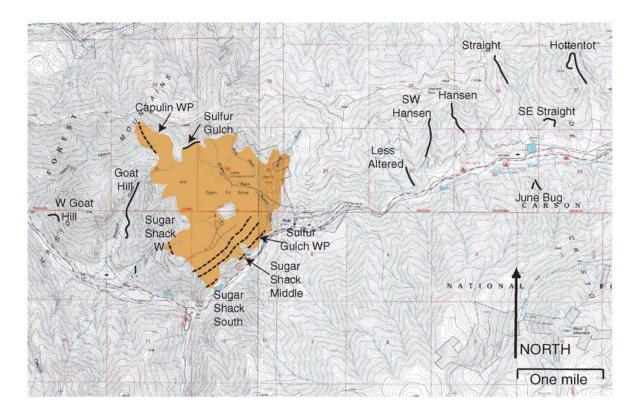


Figure 1. Map displaying composite sample traverses. Dashed lines-waste pile samples and solid lines alteration scar traverses. WP= mine waste pile



Figure 2a. Photo of Hottentot Ck. alteration scar.

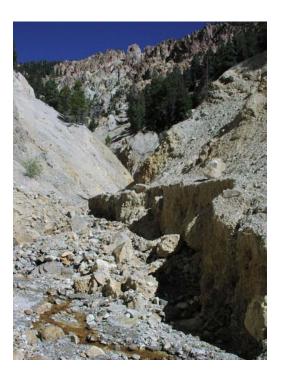


Figure 2b. Photo of the upper reach of Hansen Ck. alteration scar.



Figure 3a. Photo of upper bench of Sugar Shack South waste pile.



Figure 3b. Photo of Sugar Shack South, Sugar Shack Middle and Sulphur Gulch waste piles taken from highway near the Red River.

Laboratory Methods

Prior to laboratory analysis, a Braun vertical pulverizer equipped with ceramic plates pulverized the dried, less than 2 mm samples to 0.15 mm (100 mesh). The composite samples were decomposed in a four-acid mixture of hydrochloric, nitric, perchloric and hydrofluoric acids (Crock and others, 1983) and analyzed for forty major, minor and trace elements by inductively coupled plasma-atomic emission spectrometry (ICP-AES; Briggs, 2002). Standard reference materials were prepared along with composite samples as a measure of quality control of the analysis. Total sulfur was determined on the composite samples directly on approximately 200 mg of ground material by combustion at 1370° C in an oxygen atmosphere with infrared detection of evolved SO₂ (Brown and Curry, 2002) using a LECO Model SC-132. Composite samples were further prepared for X-ray diffraction mineralogy (XRD) in a micronizing mill to an average grain size of about 5 µm. An internal standard of Al₂O₃ with an average grain size of 1 µm was added (15% by weight) to help in the quantification of amorphous material. The XRD patterns were collected on a Scintag X-1 theta-theta diffractometer (Cu K-alpha radiation, Peltier counter) with 2mm divergence slit and 4mm scatter slit for the tube and 0.5mm scatter slit and 0.2mm receiving slit for the detector. Patterns were scanned from 4 –75 degrees 2-theta with a step size of 0.02 degrees 2-theta and a counting time of 2 s per step with a sample spinner to reduce preferred orientation. The subsequent quantitative refinements were carried out using the SIROOUANT Rietveld full-profile phase quantification program v.2, 1997 (Taylor, 1991).

Quality control for the ICP-AES technique used NIST 2711 standard reference material. NIST 2711 is a moderately contaminated soil from Montana that is a good proxy for the composited material. NIST 2711 was digested and analyzed along with the

composite samples. Table 5 shows the tabulated results from two analyses of NIST 2711. All elements reported by the technique are generally within 10 % recovery from the certified value reported for the reference material and these results are deemed acceptable.

Results and Discussion

The scar material is comprised of pyrite-enriched rocks, varying amounts of kaolinite, sericitic mica, jarosite, gypsum and other water-soluble sulfo-salts that are sources of acid rock drainage. Many of these mineral assemblages have also been identified using airborne visible-infrared imaging spectroscopy (Livo and Clark, 2002). Table 1 presents the ICP-AES and total sulfur analyses of the nine alteration scar composites and one less intensely altered composite sampled in this study. The XRD confirms that the sulfate minerals gypsum and jarosite are present in quantifiable amounts. More than 75% of the quantitative mineralogy in the alteration scar composites is made up of amorphous material, quartz and mica (probably sericite). Table 2 shows the results of the alteration scars quantitative XRD mineralogy.

The XRD showed that gypsum is more prevalent (10-12%) in Sulphur Gulch, Little Hansen Creek and Hansen Creek relative to the other scars (2-8%). The less intensely altered sample and Hottentot Creek samples showed no detectable gypsum. Similarly, Livo and Clark, 2002, reported gypsum was most abundant spectrally, in SW Hansen Creek. Jarosite was identified at 2-7% in all the scar composites, including the less intensely altered site. This is not surprising because the scars appear to be overprinted by supergene weathering as shown by the minerals gypsum, kaolinite and jarosite (Livo and Clark, 2002). Four to five percent of the scar composites are made up of the mineral kaolinite in Hansen Creek, Straight Creek and Goathill Gulch. Again, these results are consistent with Livo and Clark (2002).

The ICP-AES data of the alteration scar samples show very little chemical variation between the composites samples. Barium and Mn concentrations are approximately two times higher in the less altered sample than in the alteration scar composites. There is no conclusion to be made from this observation other than Ba and Mn are anomalous. Despite having the lowest total S concentration of 0.21 %, jarosite was detected by XRD in the less intensely altered sample.

The five mine waste piles that were sampled on the mine site are representative of 72% of the total waste rock produced (328 million tonnes). The waste piles adjacent to the Red River are up to 490 m high and are at the angle of repose (Shaw and others, 2002). Tables 3 and 4 contain the ICP-AES and XRD results of the waste pile composite samples. There is a great deal of pyrite oxidation to jarosite that can be observed by the straw-yellow color of the piles. The younger the pile (i.e., less pyrite oxidation) the more gray in color it appears. The XRD identified over 70% of quantifiable material as quartz, amorphous material and sericite (see table 4). The XRD results from the five waste piles shows that the piles are generally made up of similar minerals and in similar quantities. The amount of amorphous material is slightly lower in Sugar Shack South, Sugar Shack Middle and Sulphur Gulch than Capulin and Sugar Shack West. Also, these three piles have mixed-layer clay minerals (smectite/muscovite, smectite/illite, or montmorillonite) that is not observed in the other piles. One possible explanation for this mixed layer effect

is these piles were sampled following a storm cycle. Because sampling took place on traverses of benches and at the base, new "clay" material was transported down from the storm event. These clays are not easily differentiated by XRD due to their nondistinct, broad shaped X-ray pattern.

The ICP-AES results are similar for Sugar Shack South, Sugar Shack Middle and Sulphur Gulch and different from Capulin and Sugar Shack West, which are similar (see table 4). The variability between the two sets can most likely be explained by varying sources of waste material as the open pit was deepened and widened. Molybdenum concentrations are 30 times higher on Sugar Shack South, Sugar Shack Middle and Sulphur Gulch than Capulin and Sugar Shack West. Again, different source areas of waste material from the open pit can best explain this anomoly.

Conclusion

The composite surficial sampling of alteration scar and mine-waste pile material, represents the average properties of the area sampled. Chemical analysis by ICP-AES and quantitative XRD were performed on these samples. There are distinct chemical differences between Sugar Shack South, Sugar Shack Middle and Sulphur Gulch and Capulin and Sugar Shack West mine-waste piles. These differences can best be explained by different source rock locations within the open pit. As the pit was developed, different material was encountered and end-dumped on the various waste piles during its lifetime. Chemical distinction is not so defined between the alteration scars. The ICP-AES analysis of the nine scars showed little difference between the sample sites suggesting the scars were formed contemporaneously from similar rock types within the caldera's alteration zone. The XRD analysis is consistent with the ICP-AES results and found basically the same percentage of identified minerals in all of the scar sample composites.

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Table 1. ICP-AES and Total S results of alteration scar composites

	Hansen Ck.	SW Hansen Ck.	Straight Ck.	SE Straight Ck	Hottentot Ck.	June Bug	W Goat Hill	Goat Hill Gulch	Sulphur Gulch	Less Intensely Altered Site
Al %		6.4	6.1	6.4	6.5	6.9	7.1	5.7	6.7	6.4
Ca %		0.93	0.57	0.53	0.05	0.56	0.13	0.14	0.82	0.69
Fe %	3.4	5.1	3.6	4.4	3.3	5.0	4.8	4.7	5.6	3.5
K %		2.7	2.8	2.9	3.3	3.3	3.5	3.6	2.9	3.2
Mg %	0.58	1.3	0.96	1.0	0.58	1.1	0.64	0.38	1.0	0.91
Na %	0.41	0.88	0.49	0.79	0.19	0.52	0.6	0.38	0.84	0.81
P %	0.11	0.19	0.12	0.17	0.16	0.19	0.17	0.099	0.16	0.12
Ti %	0.23	0.15	0.12	0.15	0.11	0.13	0.2	0.12	0.19	0.31
Ag ppn	< 2	< 2	< 2	< 2	< 2	< 2	2.6	2.0	< 2	< 2
As ppn	< 10	15	< 10	< 10	12	< 10	32	14	< 10	< 10
Au ppn	< 8	< 8	< 8	< 8	< 8	< 8	< 8	< 8	< 8	< 8
Ba ppn	a 396	226	336	419	699	585	286	435	258	1050
Be ppn	a 2.5	1.6	1.9	1.5	2.0	2.6	3	2.9	2.2	3.1
Bi ppn	10 < 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Cd ppn	1 < 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
Ce ppn	n 82	62	56	63	63	48	112	89	79	88
Co ppn	1 0	9.0	7.0	7.1	5.0	15	8.5	6.7	12	18
Cr ppn		74	58	54	38	61	68	23	83	72
Cu ppn	1 22	25	42	39	20	159	99	62	100	36
Eu ppn	1 < 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
Ga ppn	1 23	18	18	20	22	19	22	22	21	20
Ho ppn	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4
La ppn	a 39	34	32	36	32	23	63	50	42	44
Li ppn	a 21	21	26	19	19	24	30	18	28	19
Mn ppn	1 299	417	373	441	152	455	802	261	408	925
Mo ppn	1 4.8	9.7	16	13	32	31	29	27	12	18
Nb ppn	19	11	12	12	15	12	32	15	11	16
Nd ppn	a 36	28	22	26	30	20	38	33	36	37
Ni ppn	1 22	18	15	12	7.4	22	19	8.0	29	39
Pb ppn	1 44	72	173	213	141	190	416	265	58	41
Sc ppn	n 6.4	8.6	6.4	7.4	6.6	8.4	8.3	5.5	9.7	8.1
Sn ppn	1 < 5	8.1	6.9	< 5	< 5	< 5	< 5	14	5.2	< 5
Sr ppn	199	626	121	228	99	304	125	101	311	213
Ta ppn	< 40	< 40	< 40	< 40	< 40	< 40	< 40	< 40	< 40	< 40
Th ppn	1 5.8	5.4	7.2	7.7	7.4	7.4	28	12	6.2	5.4
U ppn	100 × 100	< 100	< 100	< 100	< 100	< 100	< 100	< 100	< 100	< 100
V ppn	n 65	91	66	80	71	85	72	50	95	85
Y ppn	1 0	6.3	7.0	4.9	5.4	4.9	12	5.2	8.2	12
Yb ppn	1 < 1	< 1	< 1	< 1	< 1	< 1	1.8	< 1	< 1	< 1
Zn ppn		50	84	65	35	117	130	40	55	104
S %	1.39	1.92	1.15	1.15	.84	.89	1.29	1.28	1.67	.21

Table 2. Quantitative XRD results of the alteration scar composites (all results in weight percent). -, mineral not detected by XRD.

	Hansen	SW Hansen Ck.	Straight	SE Straight		June Bug	W Goat Hill		Sulphur	Less Intensely
=	Ck.	Hansen Ck.	Ck.	Ck	Ck.		· =======	Gulch	Gulch	Altered Site
Amorphous	34	21	28	20	37	28	34	21	35	31
Quartz	35	26	34	30	30	35	27	36	24	38
Mica	5	10	10	13	15	10	10	18	6	9
Jarosite	3	5	3	5	5	3	8	7	6	2
Gypsum	10	12	8	9	-	8	1	2	12	-
Pyrite	<1	-	-	-	-	-	-	-	-	-
Hematite	-	-	-	-	-	-	-	-	-	2
Plagioclase	5	9	7	10	3	6	5	7	6	5
K-spar	2	-	1	-	1	3	3	3	-	2
Chlorite	1	9	3	8	7	4	10	<1	3	2
Montmorill onite	1	8	2	5	1	1	-	2	8	2

Table 3. ICP-AES and Total S results of waste pile composites

	Sugar Shack South	Sugar Shack Middle	Old Sulphur Gulch	Capulin	Sugar Shack West
Al %	7.4	6.9	7.1	6.8	6.9
Ca %	2.3	1.9	2.1	0.41	0.39
Fe %	4.2	4.3	3.6	2.9	2.3
K %	3.2	2.8	3.3	3.2	3.4
Mg %	1.3	1.5	1.3	0.51	0.42
Na %	1.4	1.4	1.3	0.92	0.73
P %	0.16	0.16	0.15	0.055	0.046
Ti %	0.22	0.23	0.25	0.16	0.12
Ag ppm	< 2	< 2	< 2	< 2	< 2
As ppm	< 10	< 10	< 10	< 10	< 10
Au ppm	< 8	< 8	< 8	< 8	< 8
Ba ppm	704	684	680	447	397
Be ppm	3.2	3.2	3.6	2.5	2.4
Bi ppm	< 10	< 10	< 10	< 10	< 10
Cd ppm	< 2	< 2	< 2	< 2	< 2
Ce ppm	67	87	85	98	52
Co ppm	15	17	14	6.4	4.2
Cr ppm	92	100	87	29	32
Cu ppm	143	129	153	43	31
Eu ppm	< 2	< 2	< 2	< 2	< 2
Ga ppm	13	12	14	26	23
Ho ppm	< 4	< 4	< 4	< 4	< 4
La ppm	37	47	48	53	30
Li ppm	35	39	38	18	14
Mn ppm	781	751	816	561	261
Mo ppm	338	207	389	18	12
Nb ppm	11	9.9	10	40	27
Nd ppm	28	38	34	38	22
Ni ppm	41	45	39	12	8.3
Pb ppm	118	67	89	135	71
Sc ppm	10	12	10	4.9	5.4
Sn ppm	5	5	5.9	< 5	< 5
Sr ppm	560	477	505	142	142
Ta ppm	< 40	< 40	< 40	< 40	< 40
Th ppm	11	8.5	10	13	8.4
U ppm	< 100	< 100	< 100	< 100	< 100
V ppm	95	103	92	44	52
Y ppm	14	16	16	31	17
Yb ppm	1.3	1.3	1.4	3.7	2.3
Zn ppm	124	83	114	78	35
S %	2.31	2.08	1.82	.78	1.18

Table 4. Quantitative XRD results of the waste pile composites (all results in weight percent). \cdot , mineral not detected by XRD.

	Sugar Shack South	Sugar Shack Middle	Old Sulphur Gulch	Capulin	Sugar Shack West
Amorphous	17	20	21	26	23
Quartz	32	25	27	35	40
Mica	12	10	11	12	13
Jarosite	5	5	6	4	6
Gypsum	6	8	7	5	3
Pyrite	1	<1	1	<1	<1
Plagioclase	7	10	9	6	6
K-spar	6	5	5	3	4
Chlorite	8	11	10	8	3
Smectite	2	1	2	-	-
Smectite/Mica	3	3	2	-	-

Table 5. Summary of analysis results for quality control standard.

	NIST 2711	NIST 2711	Average ¹	sd ²	% R ³	NIST value ⁴
Al %	6.5	6.5	6.5	0.0	100	6.53
Ca %	2.9	2.9	2.9	0.0	101	2.88
Fe %	2.9	2.8	2.85	0.1	99	2.89
К %	2.5	2.5	2.5	0.0	102	2.45
Mg %	1.0	1.0	1	0.0	95	1.05
Na %	1.2	1.1	1.15	0.1	101	1.14
P %	0.085	0.081	0.083	0.0	-	.086
Ti %	0.27	0.27	0.27	0.0	87	0.306
Ag ppm	5	5	5	0.0	108	4.63
As ppm	100	89	94.5	7.8	90	105
Au ppm	< 8	< 8	-	-	-	-
Ba ppm	730	720	725	7.1	100	726
Be ppm	2	2	2	0.0	-	-
Bi ppm	< 10	< 10	-	-	-	-
Cd ppm	42	42	42	0.0	101	41.7
Ce ppm	79	69	74	7.1	107	(69)
Co ppm	12	10	11	1.4	110	(10)
Cr ppm	45	41	43	2.8	91	(47)
Cu ppm	110	110	110	0.0	96	114
Eu ppm	< 2	< 2	-	-	-	(1.1)
Ga ppm	16	13	14.5	2.1	97	(15)
Ho ppm	< 4	< 4	-	-	-	-
La ppm	42	38	40	2.8	100	(40)
Li ppm	27	26	26.5	0.7	-	-
Mn ppm	660	640	650	14	102	638
Mo ppm	< 2	4	4	-	250	(1.6)
Nb ppm	21	17	19	2.8	-	-
Nd ppm	33	29	31	2.8	100	(31)
Ni ppm	21	19	20	1.4	97	20.6
Pb ppm	1100	1000	1050	71	90	1162
Sc ppm	10	10	10	0.0	111	(9)
Sn ppm	5	< 5	5	-	-	-
Sr ppm	250	240	245	7.1	100	245
Ta ppm	< 40	< 40	-	-	-	-
Th ppm	13	14	13.5	0.7	99	13.6
U ppm	< 100	< 100	-	-	-	-
V ppm	82	80	81	1.4	99	81.6
Y ppm	27	27	27	0.0	108	(25)
Yb ppm	3	3	3	0.0	111	(2.7)
Zn ppm	350	320	335	21	96	350.4

¹ Arithmetic average of two analyses.
² Sample standard deviation.
³ Percent difference from certified value.
⁴ NIST values from Certificate of Analysis; values in parentheses are non-certified values.